



Enhancement of the electrochemical membrane electrode assembly in proton exchange membrane fuel cells through direct microwave treatment



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HIGHLIGHTS

- We developed a new method of direct microwave irradiation treatment to the MEA.
- Improved micropore structure was achieved using microwave treatment.
- High active site at the catalyst layer was achieved using microwave treatment.
- High Pt utilization at the catalyst layers was achieved using microwave treatment.
- The microwave-irradiated MEA show superior cell performance over non-treated MEA.

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ABSTRACT

Demonstrated herein is a novel and easily controllable method using direct microwave irradiation treatment to enhance the electrochemical structure in the membrane electrode assembly (MEA) of the fuel cell. Through direct microwave irradiation, it is found that the pore dimension changed to an improved micropore structure with a 1.5-fold larger surface area (from 9.68 to 15.21 m² g^{−1}) at the microwave power of 500 W than the rare statement, which is proportional to the mass/heat transfer properties, along with the higher interfacial site area in the electrode, for better electrochemical properties. This upgraded structure also increases the Pt catalyst utilization and reduces the electrical loss by increasing the ionic conductivity between the catalyst layer and membrane when combined with polymer electrolyte, a catalyst, and the Nafion membrane in MEA. Due to the enhancement of the MEA properties, the fuel cell performances of the microwave-irradiated MEAs show a significant improvement to 1.87 A cm^{−2} at 0.6 V over the conventional MEA performance of 1.47 A cm^{−2}. Especially achieved is a 110% enhancement in the limiting current density resulting from the developed electrochemical micropore structure.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) can convert chemical energy to electrical energy through electrochemical reaction [1–6]. For the central component of PEMFC, a membrane electrode assembly (MEA) is placed, which consists of a proton exchange membrane, two electrodes (catalyst layers), and gas diffusion layers (GDLs). These components are commonly fabricated individually and then pressed together at a high temperature and pressure [7–10]. Recently, several research groups reported

methods of designing an effective MEA by enhancing the membrane/electrode interface, considering better smooth mass transfer and a higher interfacial site area [11–13]. There have been no studies, however, on the direct treatment of the fabricated MEA.

The electrochemical reaction in the fabricated MEA can occur only at the “triple boundary phase (TBP),” where the electrolyte, reaction material, and electrically connected catalyst particles come in contact with one another. The TBP in the MEA must be required because this phase can easily transport the protons and reactants generated through the MEAs reactant to minimize the electrical losses and to enhance the electrochemical reaction for improved performance and durability. One of the most important factors to consider in the improvement of the TBP structure for better reactant transfer is the catalyst layer design. The catalyst layers at both

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the cathode and anode in the MEA typically include catalysts, catalyst supports, proton conductors, and adhesives. These catalyst layers should be highly porous to make mass transfer easier and to increase the site area for better electrochemical reaction properties [14]. Many research groups have attempted to fabricate a highly porous cathode catalyst layer with an effective structure for a high surface area and a good transfer property. Most of the studies included a pore formation step during the synthesis of the catalysts before applying them to the MEA fabrication process [15–20]. Another matter that must be taken into account for the fabrication of an effective catalyst layer is that it is also necessary to maximize the Pt utilization, which usually indicates the metal dispersion and the amount of exposed metal atoms at the TBP. Usually, the Pt utilization of the commercial Pt/C in the PEMFC appears within the range of 20–50% at the Pt particle size of 2–4 nm [21–23]. The few studies under way at research institutions focus only on the synthesis of effective catalysts that improves the metal utilization [11–13].

Along the above lines, the components of MEA have been individually synthesized to improve their electrochemical properties, and have then been fabricated together. Such kinds of catalyst or membrane preparation/treatment methods are complicated, however, as they involve many processes and thus require a long preparation time.

In this report, a new, simple approach to effective treatment is presented using direct microwave irradiation of the fabricated MEA. Microwave treatment has been used for synthesizing organic/inorganic materials, for chemical analysis, and for electrocatalysis due to its distinctive characteristics of swiftness, uniformity, simplicity, and energy saving compared with the traditional heating treatment [24,25]. To date, however, there has been no research on the electrochemical device's MEA system. Compared to a non-treated MEA, the simple direct microwave treatment of an MEA significantly increases the PEMFC cell performance by enhancing the porosity of the catalyst layers and the interface bonding between the membrane and catalyst layer, even with a short reaction time (~ 5 s).

2. Experimental

To prepare an MEA for PEMFC test, the catalyst slurry is prepared by mixing Pt/C (40 wt.%, Johnson Matthey Co.) with 5 wt.% Nafion solution in isopropyl alcohol. It is stirred for 5 min, sonicated for 3 min, and is repeated five times. The catalyst ink is sprayed onto a Nafion 212 membrane. The active electrode area for a single cell test is 1 cm^2 with Pt catalyst loading of 0.4 mg cm^{-2} for the cathode and anode. After then, the MEA is fabricated with a GDL (SGL 10BC) and catalyst sprayed membrane using hot pressing procedure at 125°C , 0.7 ton for 90 s.

The microwave system consists of microwave generator, gas controller, teflon reactor, and MEA pressing system. The prepared MEAs are placed in a teflon reactor where N_2 gas is consistently flown to avoid the combustion of the catalyst during the microwave treatment. The reactor with the sample bed is, then, applied to a multimode resonant microwave cavity. The microwave irradiation system is set at different powers (500 W, 650 W and 800 W, respectively) with a treatment time of 5 s when the frequency is fixed at 2450 MHz.

To analyze the effect of the direct microwave treatment to the MEA, the morphological characteristics of the MEAs are observed using FE-SEM (JEOL-7001F, JEOL Ltd.). Nitrogen adsorption–desorption measurements are also conducted in BELSORP (Bel, mini II) to obtain information on the surface area and pore properties.

The single PEMFC performance is measured at an operation condition of 75°C , 100% of a relative humidity. H_2/O_2 gases are supplied to the anode and cathode with a flow rate input of 100 and 150 ml min^{-1} , respectively. An activation step is operated with constant voltage at 0.6 V for 3 h. The polarization experiments are conducted using an electric load (EL500P, Daegil Electronics) and the AC impedance (0.7 V) results are analyzed using PGSTAT-30 (Autolab) to investigate the resistances in the MEAs.

3. Results and discussion

The SEM image in Fig. 1 illustrates the changes in the morphology of the catalyst layer in the MEAs resulting from the

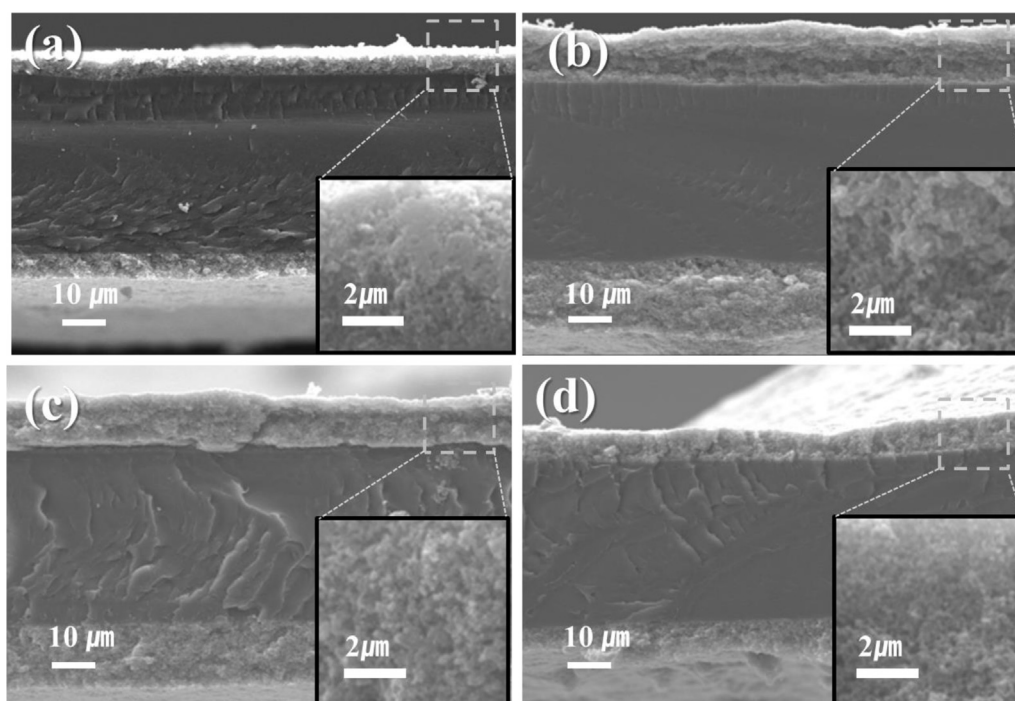


Fig. 1. FE-SEM micrographs of a cross section of the catalyst layer. (a) Non-treated MEA, and microwave-treated MEA at (b) 500 W (c) 650 W (d) 800 W for 5 s.

various microwave irradiation treatment powers. Although the catalyst amount is the same (0.4 mg cm^{-2}) for all the samples, the thicknesses of the catalyst layers are different, with values of 5.71, 14.09, 13.9, and $9.52 \text{ }\mu\text{m}$ in the order of the pristine MEA and the MEAs microwave-irradiated at 500, 650, and 800 W. These results confirm that the physical structure of the catalyst layer is modified by microwave irradiation treatment with different powers. In addition, from the image at the bottom right corner of Fig. 1, it can be seen that pores are formed in the catalyst layer through microwave radiation, even for the MEA that was microwave-irradiated at 500 W.

The aforementioned pore structure change results can be further explained by the difference in the pore properties obtained from BJH measurement. Fig. 2 shows the N_2 adsorption–desorption isotherms of the pristine MEA and of the microwave-irradiated MEAs. To focus only on the specific pore structure of the catalyst layer, the physical properties of the catalyst layer were calculated from the nitrogen adsorption–desorption measurements while the specific pore property of the rare Nafion membrane were subtracted. For all the treated samples, the isotherms exhibited the typical behavior, with rapid uptake under low partial pressures, which indicates a strong interaction between the adsorbate and the adsorbent in the macropore region [26]. The microwave irradiation at 500 W of the prepared MEA increased the amount of adsorbed N_2 , shifting the isotherms upward, which can be interpreted as an evidence for the blown pores of the catalyst layer, as can be seen in Fig. 1. This behavior resulted in a gain in the total pore volume, along with an increase in the surface site area of the catalyst layer, which can also be calculated from the isotherms. The BET surface area, total pore volume, and average pore size are summarized in Table 1. It can be clearly seen that the total pore volume incredibly increased with a similar average pore size. The highest increase ratio was 35.6% (from 0.0205 to $0.0278 \text{ cm}^3 \text{ g}^{-1}$) after 500 W microwave treatment, which was higher than the increase ratios of the MEAs after 650 and 800 W microwave treatments (9.7% and 8.3%, respectively). This result is consistent with the change in the catalyst's layer thickness as can be seen from the SEM micrographs above, indicating that the increase in thickness originated from the increased total pore volume. Furthermore, it is generally known that the surface area of catalysts increase with increased total pore volume. As the pore volume increases, the BET surface area also increases, with values of 57.1% (500 W), 46.9% (650 W), and 22.7% (800 W), through the direct microwave inducement of MEA. This modified pore structure of the catalyst layer will bring about a huge difference in the electrochemical properties and performance of PEMFC.

The amount of pores is not the only important factor for a well-designed catalyst layer; the microstructures of the catalyst layer should also be carefully considered. In Fig. 3, two distinctive pore distribution peaks, called “primary pore” and “secondary pore,”

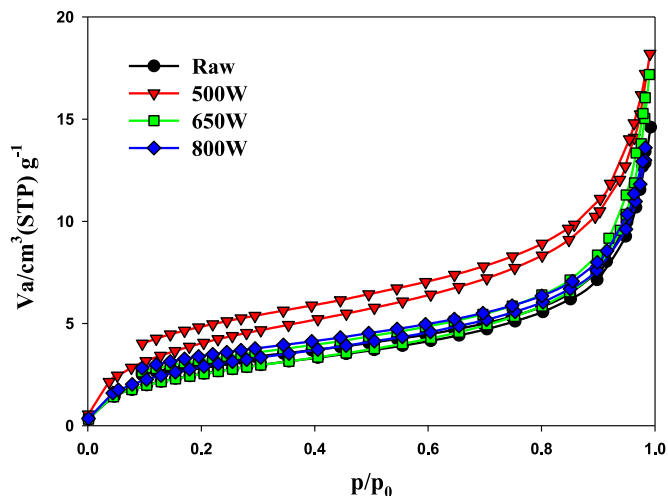


Fig. 2. N_2 adsorption–desorption isotherms of non-treated MEA and microwave-treated MEA obtained by BJH measurement.

secondary pores exist between the agglomerates and are generally larger than 40 nm [29]. Watanabe et al. reported that the primary pores work as a “reaction volume” and that the secondary pores work as main gas transfer channels in the fuel cells with electrolytes [31]. It was found that the volumes of both the primary and secondary pores increased after microwave irradiation treatment. In particular, a further increase in pore distribution was observed from all the microwave treatment power conditions. As high porosities occur due to microwave processing, this can also improve the reaction rate and increase the reacting surface of the electrocatalysts. It was clear that the microwave treatment enhanced the pore structure, which is strongly related to the MEA performance. While the primary and secondary pores of all the treated MEAs increased compared to the conventional state, the volumes of the pores decreased with radiation power increase, as confirmed by the SEM and BET data (Fig. 1). Strong energy irradiation especially after 800 W microwave treatment could make the pore structure collapse from partial burning. Even though the pores decreased with the radiation power increase, it was evident that the pore structure was improved at every microwave treatment power (500, 650, and 800 W) compared to the non-treated MEA. This improved pore structure is deeply related to the electrocatalyst surface area (ECSA), which is a crucial factor for the MEA performance.

The cyclic voltammetry curves shown in Fig. 4(a) helped to decide the ECSA of the non-treated Pt/C and the microwave-irradiated Pt/C in the H_2/N_2 system. For the calculation of ECSA from the H_2 adsorption charge on the Pt surface, the following equation was utilized [29]:

$$\text{ECSA} \left(\text{cm}^2 \text{ Pt gPt}^{-1} \right) = \frac{\text{charge} \left(\mu\text{C cm}^{-2} \right)}{210 \left(\mu\text{C cm}^{-2} \text{ Pt}^{-1} \right) \times \text{catalyst loading} \left(\text{gPt cm}^{-2} \right)} \quad (1)$$

respectively, were identified at each pore size distribution for all the MEAs [26–28]. In the top image in Fig. 3, a detailed schematic representation of the Pt/C and ionomer binder on the surfaces of the agglomerates can be seen. The primary pores are known to be formed among the primary carbon particles inside the Pt/C agglomerate and are generally smaller than 40 nm . In contrast, the

The ECSAs of the Pt/Cs microwave-irradiated at 500, 650, and 800 W were 51.46, 49.94, and $28.78 \text{ m}^2 \text{ g}^{-1}$, respectively, when the ECSA of the Pt/C was $27.29 \text{ m}^2 \text{ g}^{-1}$. The higher ECSAs of the microwave-irradiated Pt/Cs relative to that of Pt/C could be due to the increase in catalyst layer porosity. The smaller power irradiation response to the increased catalytic-activity area was

Table 1

Microstructure characteristic of the microwave-treated MEA determined from N₂ adsorption–desorption isotherms.

Electrochemical properties	Pt/C membrane	Pt/C 500 W membrane	Pt/C 650 W membrane	Pt/C 800 W membrane
BET (m ² g ^{−1})	9.68	15.21	14.22	10.88
V _{pore,total} (cm ³ g ^{−1})	0.0205	0.0278	0.0225	0.0222
Average pore diameter (nm)	9.45	7.31	9.03	8.18

confirmed. This is because the increased primary pores of the catalyst layer due to the microwave irradiation can help the gases approach the surface of the catalyst particles and increase the three-dimensional reaction interface where the catalyst, the reactant gas, and the ionomer (Nafion electrolyte) interact with one another. This catalytic behavior in the MEA can also be described by the Pt utilization (U_{pt}). The utilization of the Pt percentage was obtained from the CV results and the concept of the Pt particle size. The method that was used in this experiment considers the real surface areas of all the Pt particles, which were assumed to have uniform spherical shapes, as follows:

$$S_{pt} = \frac{\text{Surface}}{\text{mass}} = \frac{\pi \cdot D^2}{\pi D^3 / 6} = \frac{6}{\rho \cdot D} \quad (2)$$

where ρ is the mass density of Pt (21.4 g cm^{−3}) and D is the mean particle size of Pt calculated from the X-ray diffraction (XRD) patterns of each catalyst layer in the MEA [30]. The Pt particle sizes were in the typical range of 3.3–3.4 nm for all the MEAs even after the microwave treatment. They were calculated using Scherrer's equation with a shape constant (K) of 0.9 on the Pt (111) diffraction peak. The usage of the Pt can be estimated from the ratio of ECSA over the calculated S_{pt} , which expresses the amount of active surface Pt atoms for the electrochemical reactions [21,22].

$$U_{pt} = \frac{\text{ECSA}}{S_{pt}} \quad (3)$$

From theory (3), it was determined that the Pt utilization rates in the MEAs were 32.71%, 63.33%, 59.49%, and 34.80% for the raw and

500 W, 650 W, and 800 W microwave-irradiated MEAs, respectively. There was an increase in the usage of the active Pt due to the enhanced TBP. Fig. 4(b) shows the relationship between the specific surface area and Pt utilization. It can be seen that the relatively higher Pt utilization with a higher specific surface area is closely related to the electrode properties, such as enhanced TBP bonding and porous catalyst layer in the MEA. This structure definitely shows an improvement of the electrochemical property, which will also increase the PEMFC performance.

To determine the effect of microwave irradiation treatment on the electrode resistance properties, the ohmic resistance (R_{Ω}) and charge transfer resistance (R_C) of the MEA were measured via electrochemical impedance spectroscopy (EIS). This was operated at a cell voltage of 0.6 V, as shown in Fig. 5. Generally, the R_{Ω} is obtained at a high-frequency region on the real axis of semicircles, and it is influenced by the ionic conductivity through the catalyst layer and membrane as combined with the polymer electrolyte, catalyst, and Nafion membrane in the MEA. The R_{Ω} values of the untreated Pt/C MEA and of the Pt/C MEAs microwave-irradiated at 500, 650, and 800 W were 0.073, 0.072, 0.068, and 0.065 Ω cm², respectively, as summarized in Table 2. Reduced R_{Ω} values were obtained after microwave irradiation treatment due to the stronger bonding between the membrane and catalyst layer generated by the fast atomic movement in the intersection of the MEA and the slight melting of the polymer, which can produce the same effect of hot pressing during the microwave irradiation [32]. In addition, the higher microwave irradiation power induces increased agglomeration parts, which further reduce the R_{Ω} value [26,27]. This explains why the R_{Ω} value of the MEA after microwave irradiation at 800 W was much lower than that of the non-treated and other microwave-irradiated MEAs. The enhanced bonding between the slightly melted membrane/ionomer and catalysts resulted in a similar performance, as shown by the polarization curves.

Compared to the R_{Ω} , the R_C is estimated from the diameter of the semicircle. This stands for the charge transfer resistance of the interval between two intersections corresponding to the activation loss of the cell through the electrochemical reaction at the electrode [15,16]. The R_C values of the Pt/C MEA and of the Pt/C MEAs microwave-irradiated at 500, 650, and 800 W were 0.089, 0.0503,

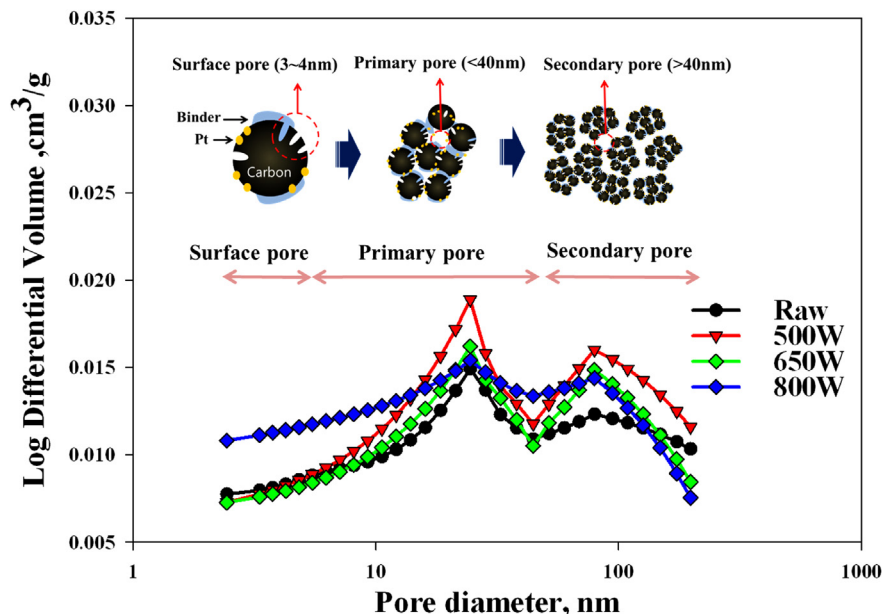


Fig. 3. Pore size distributions of non-treated MEA and microwave-treated MEA obtained by BJH measurement.

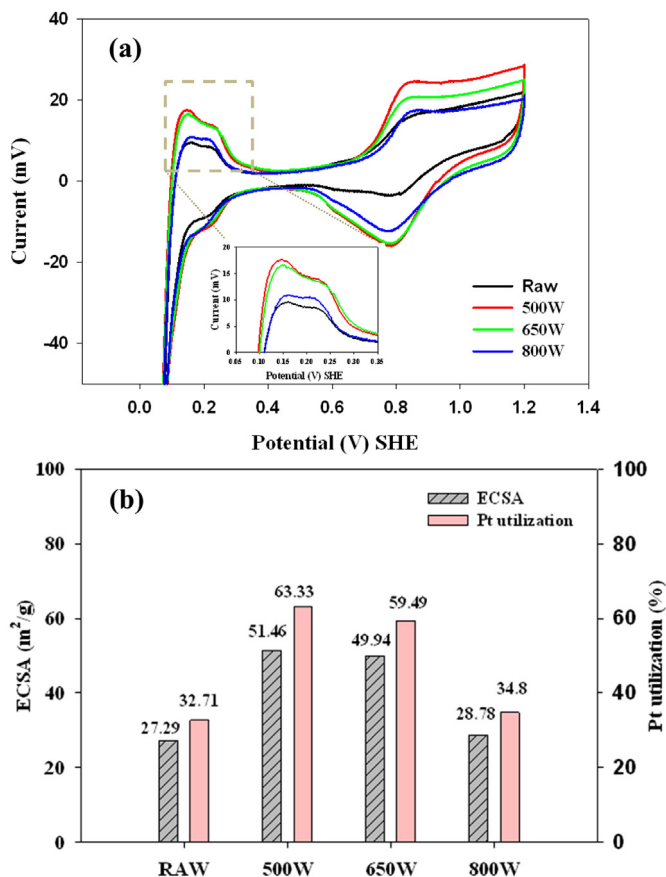


Fig. 4. Comparison of (a) cyclic voltammetry (CV) curves and (b) catalyst utilization of non-treated MEA and microwave-treated MEA.

0.0751, and 0.0708 $\Omega \text{ cm}^2$, respectively. These results confirm that the modified microstructure and configuration of the treated MEA greatly influence the reduction of the charge transfer resistance for enhanced electrochemical reaction, which is in agreement with the results of the BJH measurement and CV analysis. The reaction on the 500 W microwave-irradiated MEA especially has an excellent

Table 2

Electrochemical properties in the prepared MEA.

Electrochemical properties	Pt/C membrane	Pt/C 500 W membrane	Pt/C 650 W membrane	Pt/C 800 W membrane
R_{Ω} ($\Omega \text{ cm}^2$)	0.073	0.072	0.068	0.065
R_c ($\Omega \text{ cm}^2$)	0.089	0.050	0.075	0.071
Current density at 0.6 V (A cm^{-2})	1.47	1.87	1.85	1.80
Current density at 0.3 V (A cm^{-2})	2.71	3.75	3.65	3.60

impact with the approximately 77% reduced RC value, which is smaller than the RC value of the non-treated MEA and may provide good PEMFC performance.

Based on all the aforementioned study results, great enhancement of the PEMFC performance is expected. In Fig. 6, the fuel cell polarization performance of the Pt/C MEA is compared with those of the microwave-irradiated Pt/C MEAs. It can be clearly seen that the microwave-irradiated MEAs exhibited much better cell performances compared to the non-treated Pt/C MEA. The polarization curve in Fig. 6 shows similar activation polarization losses due to the inactive electrode kinetics of the oxygen reduction at the cathode in all the samples, but in the intermediate region, the 500 W microwave-irradiated MEA showed a decrease in slope compared to the 650 W and 800 W microwave-irradiated MEAs. This indicates that the lower-microwave irradiation power-treated MEAs had greater electrical properties due to the improved TBP attributed to the reduced resistance of the electrolyte membrane and catalyst layer, which are in good agreement with the results data on the physical characteristics and electrochemical analysis. Moreover, the limiting current is a significant value that explains the quality of the electrode. A higher limiting current density generally indicates a better mass transfer property in the MEA. As listed in Table 2, the strong effects of the lower-microwave irradiation power treatment of MEA were especially observed. While the non-treated MEA presented the lowest limiting current density (3353 mA cm^{-2}), the 500 W microwave-irradiated MEA presented the highest limiting current density (3752 mA cm^{-2}). The limiting current density value of the latter was 110% better than that of the former. Also, the 650 W and 800 W microwave-irradiated MEAs had 3653 and 3603 mA cm^{-2} current densities. These high current densities at a low voltage range demonstrate that the catalyst layer's porous structure owing to microwave treatment may greatly enhance the transfer properties of MEA. From Fig. 6, after

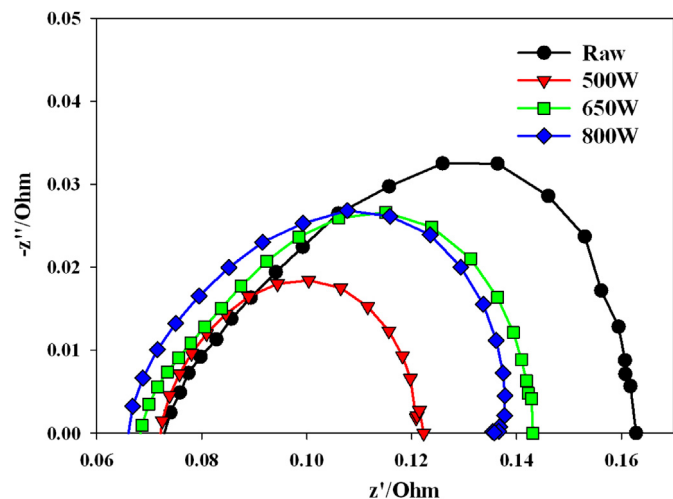


Fig. 5. Electrochemical impedance spectroscopy of non-treated MEA and microwave-treated MEA.

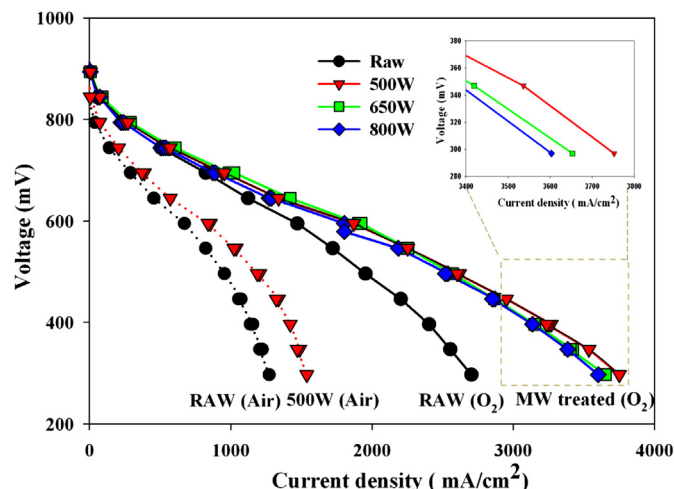


Fig. 6. Polarization curves of non-treated MEA and microwave-treated MEA.

microwave treatment, it can be seen that the mass transport at a high current density was also increased even at the air condition test. Moreover, the increase in current density was even similar with that in the oxygen condition test, where the increase values were 27% (O₂)/21% (air) at 0.6 V and 37% (O₂)/28% (air) at 0.3 V, respectively. These results obviously show the improved electrode structures of the microwave-irradiated MEAs, which had good electrochemical properties and high MEA performances.

4. Conclusion

In conclusion, a novel and easy controllable method is developed in this study to enhance the membrane electrode assembly (MEA) of the fuel cell, using microwave irradiation treatment. The use of this treatment is shown to improve the porosity of the catalyst layers, which can enhance the mass transfer in the MEA. The increased ionic conductivity between the catalyst layer and membrane is observed as combined with the polymer electrolyte, catalyst, and Nafion membrane in the MEA. The electrocatalyst surface area (ECSA) and Pt utilization (U_{Pt}) by the improved micropore structure yield higher PEMFC test performance. The fuel cell performance of the microwave-irradiated MEAs obviously increased compared to that of the non-treated MEA, even at air supply conditions. A 110% performance enhancement is especially achieved at the limiting current density after 500 W microwave irradiation for 5 s. This simple process achieves performance improvement in a very short time, showing a potential for application to the real MEA fabrication process.

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